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X-Ray Reflectivity Study of Layer-by-Layer Self-Assembled Pyrrole-Based Push-Pull Chromophores

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Beamline(s): X23B

Introduction: Design of molecule-based photonic materials represents a leading direction in the scientific quest to develop novel organic electro-optic devices promising greatly enhanced optical network speed, capacity, and bandwidth for data networking and telecommunications [1]. Layer-by-layer molecular self-assembled and templated formation of intrinsically polar arrays of high-β chromophores grown directly on silicon or related substrates requires neither electric-field poling, poling electrodes, nor electrically matched buffer layers, allowing ready device integration and reducing device design complexity. We report here the x-ray structural study of intrinsically acentric chromophoric superlattices based on high-β push-pull chromophore building blocks.

Methods and Materials: The synthesis of diethanolamine functionalized 1-(pyridine-4-yl)-2-(*N*-methyl-pyrrol-2-yl)-5-methylene-diethanolamine)ethene based dyes and the procedure for the layer-by-layer formation of intrinsically acentric multilayers on Si (111) substrates is described in reference [2]. The consecutive siloxane-based self-assembly method involves (i) benzyl iodide based "coupling layer" deposition, (ii) spin-coating of a chromophore precursor followed by vacuum oven treatment, and (iii) capping of each chromophore layer with octachlorotrisiloxane. The detailed description of the procedure of x-ray reflectivity (XRR) measurements and data treatment can be found in [3].

Results: Figure 1 shows normalized reflectivity data (R/R_F) from a typical scan on a self-assembled superlattice. Failure to fit the data assuming a uniform density film suggests that the electron density has a complicated profile. Assuming the presence of two different regions with different electron densities within the film, we have obtained good fit to our data (solid line in Fig. 1). The corresponding electron density distribution obtained from the XRR data is shown in the inset of Fig. 1. The first region, the "coupling layer", has an electron density, $\rho_{coupling}$ of ~0.33 electrons/Å^3, a thickness of ~6.5 Å, and a "molecular footprint" of ~47 Å^2. The second region, the chromophore layer, has a slightly lower electron density, $\rho_{chromophore}$, of ~0.29 electrons/Å^3, a thickness of ~9.6 Å, and a "molecular footprint" of ~57 Å^2, which is in agreement with UV-vis data [2]. It seems that about 80% of the benzyl iodide functionalities of the coupling layer have undergo a reaction with the chromophore precursor. The interfacial roughness, $\sigma_{coupling\text{-}chromophore}$, is only ~2.4 Å and the surface roughness, $\sigma_{film\text{-}air}$, ~3.1 Å, which is nearly identical to the Si(111) substrate roughness, $\sigma_{si\text{-}film}$, ~2.6 Å.

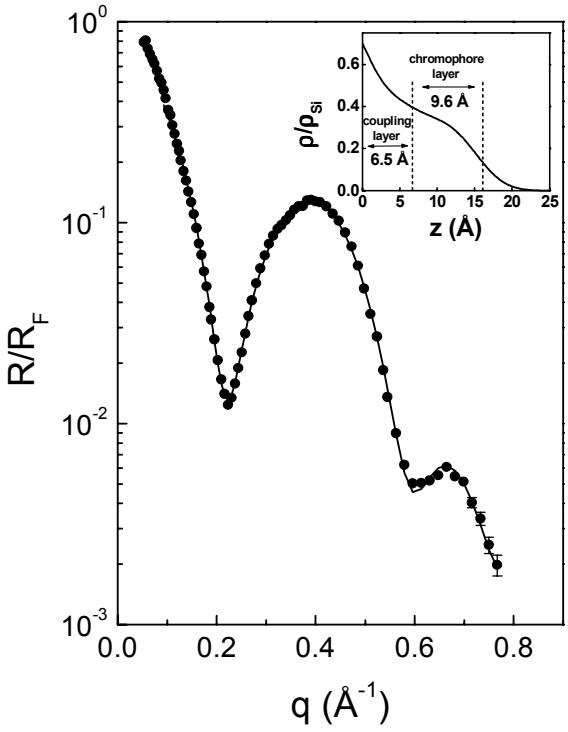

Figure 1. XRR data for a self-assembled superlattice. The solid line is the best fit to the data using the two regions model. Inset: plot of electron density relative to silicon vs distance normal to the surface.

Conclusions: We have shown that π-deficient pyridinium–ethene bridged–π-excessive pyrrole-based chromophores [2] can successfully be integrated into structurally regular, acentric multilayers. The presented results argue that the known three-step assembly method [4] may be suitable for a wide range of push-pull chromophores.

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References: [1] S.R. Marder et al, Nature **388**, 845 (1997); [2] A. Facchetti et al, to be submitted; [3] G. Evmenenko et al., J. Chem. Phys. **115**, **6722** (2001). [4] W. Lin et al, J. Am. Chem. Soc. **118**, 8034 (1996).

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